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High Yield Routes to Mo(III) Compounds by Diphenyl Silane and
Tin(II) Chloride Reduction of Mo(V) and Mo(IV) Chlorides

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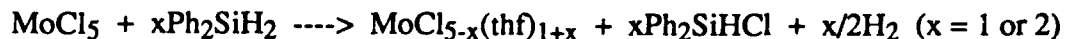
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HIGH YIELD ROUTES TO Mo(III) COMPOUNDS BY DIPHENYL SILANE AND TIN(II) CHLORIDE REDUCTION OF Mo(V) AND Mo(IV) CHLORIDES.

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Abstract-----MoCl₄(thf)₂ has been stoichiometrically reduced with SnCl₂ to form MoCl₃(thf)₃ with concomitant formation of SnCl₄(thf)₂. In an alternative procedure, MoCl₅ reacted directly with diphenylsilane according to the equation below to give high yields of either MoCl₄(thf)₂ or MoCl₃(thf)₃, depending on the reaction stoichiometry, in a single step, high yield (>85%) synthesis.



These methods avoid the possibility of over reduction that is common when metals (such as Sn or Zn) are used in heterogeneous reactions.

Introduction

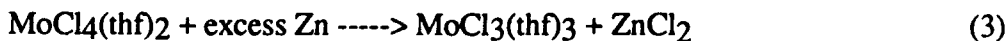
Ligated metal halide complexes of general formula MX_nL_m are valuable sources of soluble metal halides for studies of homogeneous chemical reactions. In particular, ligand exchange, association and reduction reactions of the complexes $MoCl_4(thf)_2$ and $MoCl_3(thf)_3$ have been studied extensively. A variety of methods to prepare these complexes from $MoCl_5$ with alkyl nitriles¹⁻³ to form the corresponding $MoCl_4(NCR)_2$ complexes have been studied according to the stoichiometry of equation 1. The yield of this reaction is generally 77-86%.



$MoCl_4(NCR)_2$ is converted to $MoCl_4(thf)_2$ by stirring with solvent thf with a yield of 80% as shown in equation 2.



This $MoCl_4(thf)_2$ species can then be reduced further with zinc in thf to form $MoCl_3(thf)_3$ according to equation 3.¹



However, this reaction is difficult to control and the Mo(III) product is generally contaminated with intensely coloured by-products. As an alternative, excess tin metal was used as a reducing agent,^{4,5} but control over this heterogeneous reduction is difficult.

A number of alternative homogeneous reduction methods have been reported. The compound, $MoCl_4(NCR)_2$, has been reduced with tetrakis(trimethylsilyl)hydrazine and by an



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aldehyde at 50°C according to the reaction of equation 4.³ However, the yield of this reaction was fairly low (55%) based on MoCl₄(NCR)₂ (~47% based on MoCl₅).



As part of our studies of the formation of highly dispersed metal particles, we are exploring methods of preparing highly dispersed molybdenum particles by homogeneous chemical reduction methods.⁶ Since MoCl₃(thf)₃ is a desirable starting material for these studies we sought to explore methods to prepare this compound in higher yields than currently possible.

Initial experiments focused on improving existing techniques by exerting better control over the reduction of Mo(IV) to Mo(III) using SnCl₂ as the reducing agent. While this method was successful in that over reduction of Mo(III) was not observed, the yields were only analogous to the best already reported in the literature (~70%) using other reducing agents described above. Since it is well-known from the chemical vapor deposition (CVD) literature that silane reduces high oxidation state molybdenum and tungsten halides at elevated temperatures,⁷ we investigated the reduction of MoCl₅ with diphenylsilane. These studies have resulted in a direct reduction of MoCl₅ with diphenylsilane in thf at room temperature to form MoCl₃(thf)₃ in high yield (~85% based on MoCl₅). Herein we present the results of these experiments.

Experimental Section

(i) General Procedures

All manipulations were carried out under an atmosphere of dry (molecular sieves) dinitrogen using standard Schlenk technique.⁸ All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl and stored over 4Å molecular sieves. Acetonitrile was refluxed in CaH₂ for 2hr, then was distilled and stored over 4Å molecular sieves. Pyridine (Aldrich) was dried

with molecular sieves prior to use. Molybdenum(V) pentachloride, N, N'-dimethylethylenediamine, triethylphosphine and diphenylsilane were purchased from Sigma and used without further purification. $\text{MoCl}_4(\text{thf})_2$ used in SnCl_2 reduction was prepared by using the method described in literature.¹ Elemental analyses were performed by Ms. R. Ju at the University of New Mexico, Department of Chemistry. NMR data were recorded on a Bruker AC-250P NMR spectrometer by using the protio impurities of the deuterated solvents as references for the ^1H NMR and ^{13}C resonance of the solvents as reference for ^{13}C NMR spectroscopy. Temperatures were calibrated with either ethylene glycol or methanol. ^{29}Si NMR data were recorded on the same instrument using tetramethylsilane as reference. Infrared data were recorded on a Perkin-Elmer Model 1620 FTIR spectrophotometer.

(ii). Syntheses

a. SnCl_2 reduction of $\text{MoCl}_4(\text{thf})_2$ at room temperature. We investigated the effect of

Tetrachlorobis(tetrahydrofuran)molybdenum(IV) (1.53 gram, 4.00 mmole) and tin(II) chloride (0.38 gram, 2.00 mmole) were mixed in a 100 cm^3 flask. Into this mixture, 50 cm^3 thf was transferred, resulting in a yellow suspension. After stirring for 4 hours at room temperature, a red-brown suspension was formed which was concentrated until the total volume was reduced to about 15 cm^3 . The concentrated suspension was filtered, washed with 5 cm^3 thf, then the volatile components were removed, *in vacuo*, to yield 1.02 gram of red-brown solid. The washings were combined and concentrated to a total volume of ~10 - 15 cm^3 , and after standing overnight at room temperature, another 0.10 gram of product was separated. Total yield 1.12 gram (67%).

In a separate experiment, $\text{SnCl}_4(\text{thf})_2$ was prepared by the reaction between SnCl_4 and an excess of thf. The product was characterized by elemental analysis and found to be reasonably soluble in thf (75mg/ cm^3).

Elemental analysis. Calcd for $C_{12}H_{24}O_3Cl_3Mo$: C, 34.45%; H, 5.79%. Found: C, 33.99%; H, 5.79%. IR spectra data (KBr disc): $2974cm^{-1}(m)$; $2901cm^{-1}(m)$; $1627cm^{-1}(w)$; $1455cm^{-1}(w)$; $1013cm^{-1}(m)$ and $854cm^{-1}(vs)$.

Elemental analysis. Calcd for $C_8H_{16}O_2SnCl_4$: C, 23.70%; H, 3.95%. Found: C, 23.86%; H, 3.58%. FTIR showed a characteristic absorption at 831 cm^{-1} .

b. Ligand substitution reactions

To confirm the integrity of the $MoCl_3(thf)_3$ prepared above, the derivatives $MoCl_3(PEt_3)_3$, $MoCl_3(Py)_3$ and $MoCl_3(o\text{-phenylenediamine})(thf)$ were prepared. The known compounds, $MoCl_3(PEt_3)_3$ and $MoCl_3(py)_3$ gave satisfactory analytical data. The new compound $MoCl_3(o\text{-phenylenediamine})(thf)$ was prepared according to the following procedure.

A homogeneous solution of *o*-phenylenediamine (0.62 gram, 5.74 mmole) in thf ($15cm^3$) was transferred to a stirred suspension of $MoCl_3(thf)_3$ (2.43 gram, 5.81 mmole) in thf ($20cm^3$). Immediate reaction accompanied by a colour change from red-brown to dark-brown was observed. The reaction mixture was further stirred for two hours, then was filtered and quickly washed with thf. The product, $MoCl_3(o\text{-(NH}_2)_2C_6H_4)(thf)$ was pumped dry to give 1.68 gram a yield of 76%.

Elemental analysis. Calcd for $C_{10}H_{16}N_2OCl_3Mo$: C, 31.41%; H, 4.19%; N, 7.33%. Found: C, 31.09%; H, 4.24%; N, 7.14%. IR spectra data (KBr disc): $3156cm^{-1}(s)$, $3072cm^{-1}(s)$, $2972cm^{-1}(s)$, $2876cm^{-1}(s)$, $1624cm^{-1}(w)$, $1563cm^{-1}(s)$, $1497cm^{-1}(s)$, $1294cm^{-1}(w)$, $1231cm^{-1}(w)$, $1133cm^{-1}(s)$, $1043cm^{-1}(s)$, $885cm^{-1}(m)$ and $762cm^{-1}(m)$.

c. Ph_2SiH_2 reduction of $MoCl_5$ to form $MoCl_3(thf)_3$

Diphenylsilane (12.20 gram, 66.3 mmol) was dissolved in 50 cm^3 of thf. To this solution, 9.00 gram (33.0 mmol) of $MoCl_5$ was added slowly with rapid stirring at room temperature. An exothermic reaction was observed and a yellow solid formed immediately. All the $MoCl_5$ was added over ~20 minutes and during this time gas evolution was observed. On continued stirring the colour deepened until after 4hr, a red-brown suspension was formed. The stirrer was stopped and the

solution was filtered and washed twice with thf (10 cm³) to give 11.20 gram of MoCl₃(thf)₃ in 85% yield based on MoCl₅. Alternatively, in a reverse addition experiment, diphenylsilane was added to a suspension of MoCl₅ in pentane cooled by an ice/NaCl/water bath to ~-10°C. Initially, a yellow solid was formed. However, continued stirring at room temperature for 48 hours, resulted in separation of a red-brown solid in 85% yield based on MoCl₅.

The crude product gave satisfactory elemental analysis data, calcd for C₁₂H₂₄O₃Cl₃Mo: C, 34.45%; H, 5.79%. Found: C, 34.11%; H, 6.09%. The IR data consistent with authentic MoCl₃(thf)₃. The silicon by products show ¹H NMR chemical shifts at 5.77ppm (J_{H-Si}=235Hz) (major), 5.04ppm (J_{H-Si}=198Hz) (minor), 5.85ppm (J_{H-Si}=218Hz) (minor); Proton decoupled ²⁹Si NMR chemical shifts at -5.63ppm (major) (pentet of doublet with J_{H-Si}=235Hz and J_{H-Si}=~6Hz), -33.69ppm (minor) (pente: of triplet with J_{H-Si}=198Hz and J_{H-Si}=~6Hz), -18.98ppm (minor) (pentet of doublet with J_{H-Si}=218Hz and J_{H-Si}=~6Hz).

d. Ph₂SiH₂ reduction of MoCl₅ to form MoCl₄(thf)₂

According to the procedure described in c above, 9.45 gram (34.62 mmol) of MoCl₅ was reacted with one equivalent, 6.40 gram (34.78 mmol), of diphenylsilane dissolved in 75 cm³ of thf resulting in a formation of a purple-yellow suspension. After about 20min. the solution was filtered and washed with three 10 cm³ portions of thf. The compound MoCl₄(thf)₂, 9.00 gram was obtained, a yield of 68% based on MoCl₅.

Elemental analysis. Calcd for C₈H₁₆O₂Cl₄Mo: C, 25.13%; H, 4.22%. Found: C, 24.93%; H, 4.06%. The IR data is consistent with authentic MoCl₄(thf)₂. The silicon by products show only one ¹H NMR chemical shift at 5.77ppm with two satellites separated by 235Hz.

Results and Discussion

SnCl₂ reduction: The use of stoichiometric amount of SnCl₂ as a reducing agent reduces MoCl₄(thf)₂ forming MoCl₃(thf)₃ according to the reaction shown in equation 5.

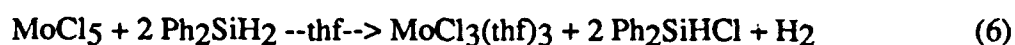


The reaction shown in equation 5 has the advantage of homogeneous stoichiometric reduction and avoids the possibility of over-reduction that is encountered when metallic tin is used. The red-brown MoCl₃(thf)₃ solid was separated in a yield 70% based on MoCl₄(thf)₂, or about 45% based on MoCl₅, which is analogous to the best yields of MoCl₃(thf)₃ reported in the literature.⁴ To confirm the integrity of the MoCl₃(thf)₃ prepared by this method, several derivatives were prepared by ligand substitution reactions including the known species MoCl₃(PEt₃)₃, MoCl₃(Py)₃⁹ and a new complex, MoCl₃(*o*-(NH₂)₂C₆H₄)(thf) which was formed by reacting MoCl₃(thf)₃ with one equivalent of *o*-phenylenediamine in thf solution. These compounds were characterized by elemental analysis and IR spectroscopy.

One problem associated with this method is the relatively low solubility of the reaction product, SnCl₄(thf)₂, in thf (see Experimental section) formed during the reaction of equation 5. This can result in trace contamination of MoCl₃(thf)₃ when isolated by filtration. The two species, MoCl₃(thf)₃ and SnCl₄(thf)₂, can be distinguished by their characteristic IR bands at 854 and 831 cm⁻¹, respectively. Even though the amount of SnCl₄(thf)₂ contamination was below the detection limit of our IR instrument, the presence of tin could be observed in subsequent experiments.⁶ Changing to a solvent in which SnCl₄(thf)₂ has higher solubility may result in a better separation, but also leads to rearrangement of MoCl₃(thf)₃. For example, MoCl₃(thf)₃ decomposes in benzene¹ and dimerizes in methylenechloride forming a number of different thf coordinated dimers.¹⁰⁻¹² So, although this synthetic modification prevents over reduction that is common in the reaction of equation 3, it does not result in higher yields of MoCl₃(thf)₃ compared to those reported in the

literature. Furthermore, this method still involves three steps starting from MoCl_5 . Therefore, we sought an alternative synthetic method to avoid these problems.

Ph_2SiH_2 reduction: Formation of $\text{MoCl}_3(\text{thf})_3$: Direct reduction of MoCl_5 with diphenylsilane in thf produced $\text{MoCl}_3(\text{thf})_3$ in high yield (85%) based on MoCl_5 as described by equation 6.



The $\text{MoCl}_3(\text{thf})_3$ formed was separated by filtration and purified by washing with thf to remove all the silicon containing by-products were removed.

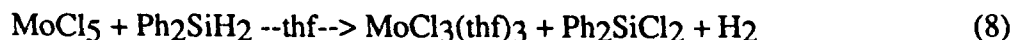
The silicon products were isolated by evaporating the solvents from the washings *in vacuo*. Both ^1H NMR and ^{29}Si NMR show that Ph_2SiHCl is the main silicon component. The ^1H NMR resonance at 5.77 ppm with $^1J_{^{29}\text{Si}-^1\text{H}} = 235\text{Hz}$ was assigned to Ph_2SiHCl by comparison to the data for pure Ph_2SiHCl . This assignment was confirmed by proton decoupled ^{29}Si NMR spectroscopy which showed a resonance at $\delta = -18.98\text{ppm}$ which was split into two pentets in the proton coupled ^{29}Si NMR due to the one-bond Si-H coupling (235Hz) and coupling to four three-bond aryl protons ($\sim 6\text{Hz}$). These data are identical to authentic Ph_2SiHCl . A small amount of Ph_2SiH_2 was also identified in the pentane extract by ^1H and ^{29}Si NMR spectroscopy. Evidence for the presence of a trace amount of another species was observed which exhibited a ^1H NMR resonance at $\delta = 5.85\text{ppm}$ with $^1J_{^{29}\text{Si}-^1\text{H}} = 218\text{Hz}$, and a ^{29}Si resonance at $\delta = -18.89\text{ppm}$ which was split into a doublet of pentets (218Hz, $\sim 6\text{Hz}$) in the proton coupled silicon spectrum. These data are consistent with a species with a general formula of Ph_2SiHX . In an attempt to identify X, $[\text{Ph}_2\text{SiH}]_2$ was prepared by lithium reduction of Ph_2SiHCl , and $\text{Ph}_2\text{SiH}(\text{O}-i\text{-Pr})$ was prepared by reaction of $\text{Na}(\text{O}-i\text{-Pr})$ with Ph_2SiHCl in thf. However, neither product gave ^1H or ^{29}Si resonances that exactly matched those of the unidentified resonance, although those of $\text{Ph}_2\text{SiH}(\text{O}-i\text{-Pr})$ ($\delta = 5.87\text{ppm}$ with $^{29}\text{Si}-^1\text{H}$ coupling of $J = 218\text{Hz}$ and ^{29}Si NMR $\delta = -20.71\text{ppm}$) were very similar.

Ph₂SiH₂ reduction: Formation of MoCl₄(thf)₂: When using two equivalents of Ph₂SiH₂ to reduce MoCl₅, a yellow solid was observed as an intermediate during the early stages of the reaction. An IR spectrum of this yellow solid, showed a strong absorption at 810cm⁻¹, consistent with formation of MoCl₄(thf)₂. An experiment in which one equivalent of Ph₂SiH₂ was reacted with MoCl₅ resulted in formation of MoCl₄(thf)₂, as shown in equation 7 below.

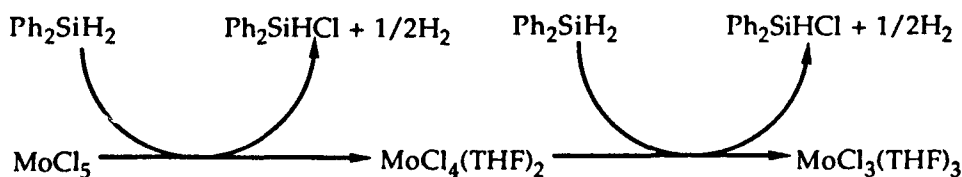


The yellow product formed was easily separated by filtration and washed with thf. The identity of MoCl₄(thf)₂ was confirmed by IR and elemental analysis. The silicon containing products were analyzed by ¹H and ²⁹Si NMR spectroscopy and revealed the presence of only Ph₂SiHCl as the by-product.

It is interesting to note that no evidence for Ph₂SiCl₂ was observed in any of these reactions. This rules out a reaction according to equation 8,



and implies that the intermediate, Ph₂SiHCl, is a less potent reducing agent than Ph₂SiH₂. In separate experiments, no reaction was observed between Ph₂SiHCl and MoCl₄(thf)₂ in thf at room temperature. As a result, the reduction of MoCl₅ may be written according to Scheme 1 where two equivalents of Ph₂SiH₂ are necessary and MoCl₄(thf)₂ is produced as an intermediate.



Scheme 1

Further experiments are in progress to determine whether $\text{MoCl}_3(\text{thf})_3$ can be reduced further with silane reducing agents.

Acknowledgements -----We thank the Office of Naval Research, Chemistry and Department of Materials Research for funding this research (ONR N00014-91-J-1258) and the National Science Foundation Chemical Instrumentation program for the purchase of a low-field NMR spectrometer.

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